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QCM and Electrochemical Studies of Li Intercalation in V_6O_{13}

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Murphy et al.(1) first demonstrated that vanadium oxides, particularly nonstoichiometric V_6O_{13} , have a large reversible insertion capacity and high theoretical energy density, making vanadium oxides attractive cathode materials in secondary lithium batteries(2-5). This capacity is primarily due to the open channel structure of V_6O_{13} through which cations diffuse to reside on sites within the cavities. Previous work on Li(7,8), Na(8), Zn(8), and Cu(8) in V_6O_{13} single crystals has demonstrated high reversibility at low intercalant concentrations. Despite the impressive properties of V_6O_{13} , a loss of faradaic capacity has been observed in the early charge-discharge cycles(5,6) which has not been explained satisfactorily.

Recently, the quartz crystal microbalance (QCM) was introduced to determine *in situ* mass changes of electrodes used for concurrent redox processes and ion insertion in conducting and redox polymers (9-13), for inorganic hexacyanometallate films (14), and for aging effects in WO_3 (15). The latter paper is the only previous QCM study of intercalating oxides. Recent reviews by Ward and Buttry(16), Deakin and Buttry(17), and Smyrl and Naoi(18), have described other work with the QCM. The purpose of the present communication is to report results of the measurements of electrochemical intercalation of Li and the attendant mass change in thin films of V_6O_{13} . It was found that at low and modest concentrations of the intercalants, the stoichiometry of the reaction is simple metal ion insertion, and the measured mass (QCM) is equal to mass (charge) calculated from the charge passed. At higher concentrations, the ratio of mass (QCM)/mass (charge) is larger than one, and suggests other complexities such as changes of morphology and the formation of second phases.

Chemicals used in this study were all reagent grade. Lithium perchlorate (Fluka) was dried in a vacuum oven for a day at 120°C. Propylene carbonate (Fluka, 0.005 percent water content) was used as received. Instrumentation of the QCM has been described previously(13). Shear mode 6 MHz AT-cut quartz crystals(Inficon) were used for the investigation. Mass change(Δm , gm) was calculated from the Sauerbrey(19) mass- frequency relationship in liquid:

$$\Delta f = - \frac{2f_0^2 \Delta m}{\sqrt{\rho_q \mu_q} A}$$

where Δf is the measured frequency change(Hz); f_0 is the fundamental frequency of quartz crystal(Hz); A is the electrochemically and piezoelectrically active surface area of the quartz crystal(0.33 cm²); ρ_q is density of quartz(2.648 g/cm³); μ_q is shear modulus of quartz (2.947×10^{11} g/cm-s²).

Nonstoichiometric polycrystalline V_6O_{13} was prepared by thermal decomposition of NH_4VO_3 as described previously(5). TGA confirmed the stoichiometry to be between $V_6O_{13.45}$ and $V_6O_{13.11}$. This product was ground to a fine powder, and a slurry of the particles in acetone (Mallinckrodt) was deposited on a quartz crystal (coated with nickel) studies and cured overnight in a vacuum oven at 80°C. The mass of deposited V_6O_{13} was

measured independently and used to calculate cation compositions at each level of intercalation. The quartz plate was sealed to the glass cell with a silicone rubber sealant. The grain size of V_6O_{13+y} was about 0.4-0.6 μm , and the film thickness was about 1 μm by SEM. The projected area of the electrode was 0.33 cm². The electrolyte solution was purged with argon gas to avoid side reactions with oxygen. The gas tight electrochemical cell was assembled in an argon filled glove box, filled with ~5 ml of electrolyte, and transferred to the laboratory. A three-electrode system was used for electrochemical control of the intercalation. Li was used for both reference and counter electrodes in the cell.

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Linear sweep voltammetry measurements were used for charge insertion or removal. Simultaneously, mass changes were measured with the QCM. The cell was maintained at a constant potential (3.0 V vs. Li) for several hours to equilibrate the cation-free oxide with the electrolyte at the start of each experiment.

A typical cyclic voltammogram of polycrystalline V_6O_{13}/Li obtained in three voltage ranges [(A) 3.0-2.7 V, (B) 3.0-2.4 V, (C) 3.0-1.9 V] at a sweep rate of 0.1 mV/s is presented in Fig. 1. Background current was measured on a bare nickel electrode and was negligible in the voltage range of 3.0 to 1.9 V vs Li. At voltages more negative than 2.5 V, lithium intercalation/deintercalation in V_6O_{13} lattice occurs with a double peak at 2.75 V, and additional peaks at 2.55 V, and 2.05 V with respect to Li, corresponding to sequential filling of lithium at different sites as reported previously(4).

Simultaneously, mass measurements with the QCM were performed and compared to those calculated from the integrated charge passed during linear sweep voltammetry, and the results are shown in Fig. 2. Charge and mass curves agree well in the composition range of $0 < x < 1$, corresponding to the voltage range 3.0 to 2.7 V (region A). Therefore, the stoichiometry in this range is expressed by:



Repeated cycling in this range demonstrated that the insertion process was 100% reversible, and the peaks were constant for all cycles. The first few cycles showed a small hysteresis in the QCM curves, with an indication that mass inserted was not removed, even though there was always charge reversibility as noted above. The hysteresis disappeared after about eight conditioning cycles, and thereafter the mass at the end of an individual cycle was always equal to that at the beginning. The hysteresis was apparently caused by a net change of morphology of the film (i.e., crystal packing, roughness) during the conditioning process as the structure swelled and contracted. During intercalation/deintercalation, Murphy et al.(6) demonstrated by x-ray diffraction (XRD) that the lattice swells and contracts as Li^+ is inserted and removed respectively. Schumacher, Gordon, and Melroy(20) have previously shown that small changes in surface morphology also cause changes of apparent mass of a QCM immersed in a liquid because different amounts of liquid are entrained with the rough surface.

After cycling a film to steady state (~8 cycles) in region A, it was then cycled in the range 3.0 to 2.40 V (region B). It showed approximate equality of mass (QCM) to that calculated from the charge, so that the stoichiometry of the insertion reaction was given as above. However, repeated cycles showed a decrease of charge in each of the cathodic and anodic peaks with each succeeding cycle. The decreased charge capacity could not be recovered by cycling between 3.3 and 2.7 V after cycling in region B. The swelling and contraction in region B apparently caused loss of electrical contact between some of the solid particles with subsequent loss of capacity.

The ratio of mass (QCM)/mass (charge) approached 3 in the range from 2.40 to 1.9 V, indicating a large change of morphology and perhaps second phase formation in this region. There is additional loss of capacity with repeated cycling in the region C, evidenced by lower currents and shifting peak positions at 2.5 and 2.75 V. The lost capacity could not be recovered. Further study is underway to clarify the processes in this region.

In summary, it was found that Li intercalation involved one lithium ion for each electron up to lithium compositions of 1. At higher lithium compositions ($x > 1$), there is significant departure of the measured mass from that calculated from the charge passed. Morphology changes apparently caused the deviation. The results indicate that an extension of the QCM to powdered, compact films is feasible, and may permit a wide range of electrode materials to be

studied. To extend the measurements to include systems that change morphology, however, simultaneous morphology change measurements will have to be made. Such measurements are underway in our laboratories.

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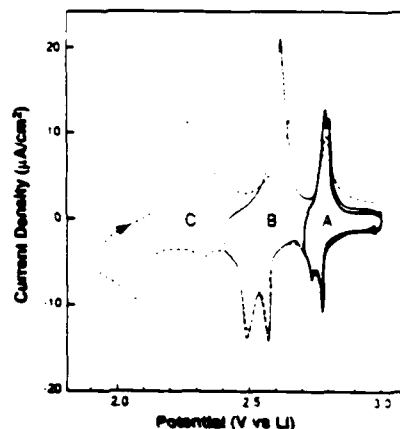


Fig. 1 Cyclic Voltammogram of V_6O_{13}/Li in $LiClO_4$ /propylene carbonate; sweep rate: 0.1 mV/s; at 25°C. Note: Curves for Sweeps in Regions A, B, and C respectively.

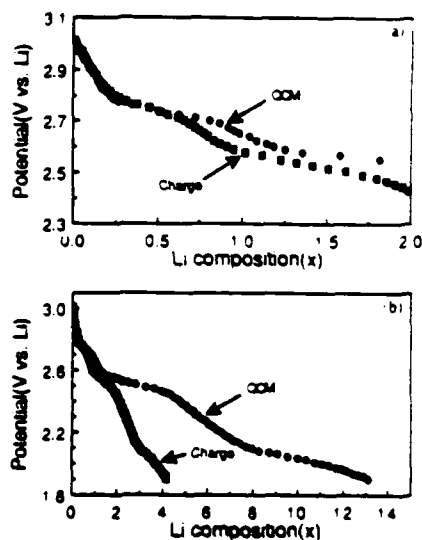


Fig. 2 Comparison of Mass (QCM) and Mass (charge) for Li^+ insertion into V_6O_{13} from $LiClO_4$ /propylene carbonate solutions: (a) Region where Mass(QCM)/Mass(charge) = 1; (b) Region where Mass(QCM)/Mass(charge) > 1.

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